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Molecular force field for thionyl and sulphuryl fluorides

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The potential energy constants of thionyl fluoride and sulphuryl fluoride were calculated using a Urey-Bradley force field and taking into account the presence of the lone pair of electrons. Mean vibrational amplitudes, Coriolis coupling constants, rotational distortion constants and the thermodynamic properties were also evaluated.

INTRODUCTION

In the earlier investigations by Ramaswamy & Jayaraman (1970, 1971, 1972) the potential energy constants of seleninyl and selenonyl fluorides, seleninyl, thionyl and sulphuryl chlorides and thionyl bromide were calculated taking into account the presence of the lone pair of electrons Here such a study has been extended to thionyl and sulphuryl fluorides.

SPECTRAL DATA AND MOLECULAR PARAMETERS

The Raman spectrum of SOF_2 was first investigated by Best & Trampe (1938) who reported six fundamental frequencies. A Raman spectrum study by Goehring (1947) of a number of sulfoxy acids and their derivatives included a spectrum of thionyl fluoride with six lines which appeared to confirm the results of Best & Trampe. Subsequent work by O'Loane & Wilson (1955) on the infrared spectrum and by Bender & Wood (1955) on the Raman spectrum showed only five fundamentals and failed to confirm the lowest frequency line at 326 cm^{-1} observed by previous investigators. O'Loane & Wilson assigned for the missing fundamental mode a value of 410 cm^{-1} from an analysis of combination modes. Gillespie & Robinson (1961) on the basis of the comparison of molecules with similar vibrational modes rejected the value 410 cm^{-1} in favour of 326 cm^{-1} for ν_4. Recently Seel & Budeny (1965) reported the infrared spectrum. The latest work on SOF_2 is due to Pace & Samuelson (1966). They made a thorough investigation of the infrared and Raman spectra of thionyl fluoride under fairly high resolution and

reported perhaps the most accurate and reliable values of fundamental vibrational frequencies. In the present work their values were made use of in the calculations.

The Raman and the infrared spectra of SO_2F_2 were reported by Perkins & Wilson (1952), Bender & Wood (1955), Hunt & Wilson (1960) and Gillespie & Robinson (1961) and several conflicting assignments for this molecule have veen proposed. Lide *et al* (1965) made the microwave measurements of SO_2F_2 to include higher vibrational levels and examined the infrared matrix spectrum of SO_2F_2. They gave a reliable vibrational assignement for SO_2F_2 on the basis of a C_{2v} model. Later Birchall & Gillespie (1966) confirmed the assignment of the fundamental frequencies given by Lide *et al*. The structural parameters and the vibrational frequencies used in the present study for both the molecules are presented in tables 1 and 2, respectively.

Table 1. Molecular parameters of SOF_2 and SO_2F_2

Molecule	S—O (Å)	S—F (Å)	$\widehat{FSF}$	$\widehat{FSO}$	$\widehat{OSO}$	Ref.
SOF_2	1.412	1.585	92°49′	106°49′	—	Ferguson (1954)
SO_2F_2	1.405	1.530	96°7′	108°18′	123°58′	Lide *et al* (1957)

Table 2. Observed and calculated wave numbers for SOF_2 and SO_2F_2

SOF_2					SO_2F_2					
	Obs.	13299,	808.2,	530.4,	377.8		Obs.	1269,	848,	544, 384	
A′	Calc.	1329,	809,	527,	381	A_1	Calc.	1269,	848,	546, 390	—
							Obs.	388			
						A_2	Calc.	402			
	Obs.	747.0,	392.5				Obs.	1502,	553		
A″	Calc.	748,	396.			B_1	Calc.	1502,	545		
							Obs.	885,	539		
						B_2	Calc.	885,	520		

Potential Energy Constants

The internal coordinates and symmetry coordinates used here werees sentially the same as those given earlier and the constants a, b, c and d occuring in the symmetry coordinates of SO_2F_2 have the following numerical values :

$$a = 0.7357 \qquad c = -0.5216$$
$$b = 1.2431 \qquad d = 1$$

The force field calculations for SOF_2 and SO_2F_2 were carried out as outlined earlier, (Ramaswamy & Jayaraman 1970). The calculated force constant values are given in tables 3 and 4.

Table 3. Potential energy constants of SOF_2

F^0 matrix elements[a] in symmetry coordinates		Modified UBFF constants in internal coordinates		Modified UBFF constants	
F_{11}^0	11.4820[b]	$\bar{f}_D$	11.4820	$\overline{K}_D$	10.7437
F_{22}^0	5.0147	$\bar{f}_d$	4.4567	$\overline{K}_d$	3.5634
F_{33}^0	1.7257	$\bar{f}_\alpha$	1.2582	$\overline{H}_\alpha$	0.9845
F_{44}^0	2.1433	$\bar{f}_\beta$	2.5609	$\overline{H}_\beta$	2.0461
F_{12}^0	0.6283	$\bar{f}_{dd}$	0.5579	$\overline{F}_{FF}$	0.9752
F_{13}^0	0.5517	$\bar{f}_{Dd}$	0.4442	$\overline{F}_{0F}$	0.6551
F_{14}^0	−0.3901	$\bar{f}_{D\alpha}$	0.3130	$\overline{F}_{0\alpha}$	0.7219
F_{23}^0	0.5631	$\bar{f}_{d\alpha}$	0.2513	$\overline{F}_{Dd}$	−0.0514
F_{24}^0	0.3610	$\bar{f}_{d\beta}$	0 4383	$\overline{F}_{dd}$	0.0237
F_{34}^0	0.2636			$\overline{F}_{D\alpha}$	0.0822
F_{22}^0	3.8988				
F_{99}^0	1.2082				
F_{89}^0	0.2513				

(a)—The F^0 matrix elements containing only stretching constants are in mdynes/Å, those containing only angle angle constants are in mdynes Å/rad^2 and those containing bond angle interaction constants are in mdynes/rad.

(b)—This number of significant figures is retained to secure internal consistency in the calculations

Table 4. Potential energy constants of SO_2F_2

F^0 matrix elements[a] in symmetry coordinates		UBFF constants in internal coordinates		UBFF constants	
F_{11}	12.6707[b]	f_D	12.2583	K_D	11.0954
F_{22}	5.6389	f_d	5 3557	K_d	4.3023
F_{33}	1.5563	f_α	1 0770	H_α	0.9234
F_{44}	1.3911	f_β	1 7243	H_β	1.2347
F_{12}	0.9043	f_γ	1 0713	H_α	1.4043
F_{13}	0.1383	f_{DD}	0.4123	F_{FF}	0.9752
F_{14}	−0.5310	f_{Dd}	0 5831	F'_{OF}	0.6551
F_{23}	−0.5310	$f_{D\delta}$	0.4522	F'_{OO}	0.5145
F'_{24}	−0.1720	$f_{D\alpha}$	0.1920		
F'_{34}	−0.2299	$f_{D\alpha}$	0 4363		
F_{55}	1.4365	$f_{D\gamma}$	0 3020		
F_{66}	11 8460	$f_{d\gamma}$	0 2577		
F_{77}	1.6713				
F_{67}	0.4271				
F_{88}	5 0726				
F_{99}	2.0713				
F_{89}	0 3644				

(a), (b)—As given in table 3.

Mean Vibrational Amplitudes, Rotation Distortion and Coriolis Coupling Constants

The mean square vibrational amplitudes, rotational distortion constants and Coriolis coupling constants were evaluated using the relations given by Cyvin (1959), Kivelson & Wilson (1952) and Meal & Polo (1956), respectively. Important mean amplitude quantities, rotation distortion constant values and Coriolis coupling constants are given in tables 5, 6 and 7, respectively.

Table 5. Mean vibrational amplitudes (Å) for SOF_2 and SO_2F_2 at 298.16°K

Molecules \ Distances	S—O	S--F	F...F	O....F	O...O	Reference
SOF_2	0.0344	0 0437	0.0629	0.0785	-	Present work
	0.0346	0 0441	0 061	0.069	-	Muller *et al*, (1968)
	0.03945	0 04354	0 07720	0 07654	-	Venkateswarlu & Rajalakshmi (1965)
SO_2F_2	0.0338	0.0410	0 0584	0 0608	0.0632	Present work
	0 0339	0.0406	0 0599	0 0601	0.0604	Cyvin & Hargittai (1969)
	0.03969	0 04282	0 06612	0 05476	0.05830	Venkateswarlu & Malathy Devi (1965)

Table 6. Rotational distortion constants (kHz) of SOF_2 and SO_2F_2

Constants \ Molecules	SOF_2	SO_2F_2
D_J	4.806	3 169
D_K	3.970	−0.290
D_{JK}	−3.841	−1.047
R_5	−1.104	−0.246
R_6	0.048	0.129
δ_J	−1.286	0.368

Table 7. Coriolis coupling constants of SOF_2

Coupling species		ζ_{ij}^{x}*	Coupling species		ζ_{ij}^{y}	Coupling species		ζ_{ij}^{z}
$A'\times A''$	ζ_{15}	−0.186	$A'\times A'$	ζ_{12}	−0.270	$A'\times A''$	ζ_{15}	−0.361
	ζ_{25}	0.360		ζ_{13}	0.576		ζ_{25}	−0.003
	ζ_{35}	−0.724		ζ_{14}	−0.409		ζ_{35}	0 454
	ζ_{45}	−0.539		ζ_{23}	−0.345		ζ_{45}	−0.433
	ζ_{16}	0.566		ζ_{24}	0.365		ζ_{16}	0.690
	ζ_{26}	−0.264		ζ_{34}	−0.370		ζ_{26}	−0.196
	ζ_{36}	0.122					ζ_{36}	−0.422
	ζ_{46}	−0.566	$A''\times A''$	ζ_{56}	−0.272		ζ_{46}	−0.229
$A_1\times B_2$	ζ_{18}	0.390	$A_1\times B_1$	ζ_{10}	−0.392	$A_1\times A_2$	ζ_{15}	0 548
	ζ_{28}	−0.394		ζ_{26}	0.356		ζ_{25}	−0.218
	ζ_{38}	−0.448		ζ_{36}	0.839		ζ_{35}	0.677
	ζ_{48}	0.682		ζ_{46}	−0.110		ζ_{45}	−0.438
	ζ_{19}	0.517		ζ_{17}	0.588	$B_1\times B_2$	ζ_{68}	0.607
	ζ_{29}	−0.304		ζ_{27}	−0.396		ζ_{69}	0.691
	ζ_{39}	−0.362		ζ_{37}	0.389		ζ_{78}	−0 620
	ζ_{49}	−0.723		ζ_{47}	0 551		ζ_{79}	0.106
$A_2\times B_1$	ζ_{56}	−0.226	$A_2\times B_2$	ζ_{58}	−0.286			
	ζ_{57}	−0.449		ζ_{59}	0.415			

* $\zeta_{ji}^{\alpha} = -\zeta_{ij}^{\alpha}$

Thermodynamic Properties

The thermodynamic properties *viz*, heat content, free energy, entropy and heat capacity are calculated for SOF_2 and SO_2F_2 at 8 temperatures between 298.16° and 1000°K at one atmosphere for the ideal gas state and for the rigid rotor, harmonic oscillator approximation. The calculated values are presented in table 8.

Table 8. Heat capacity C_p, heat content H, free energy F and entropy S in cal deg^{-1} mole^{-1} for SOF_2 and SO_2F_2

Molecule	$T°K$	$C_p°$	$\left(\frac{H°-E_0°}{T}\right)$	$-\left(\frac{F°-E_0°}{T}\right)$	$S°$
SOF_2	298.16	13.65	10.12	56.90	67 02
	400	15.37	11.25	60 04	71.29
	500	16.51	12.20	62.66	74.86
	600	17.30	12 99	64 95	77 98
	700	17.85	13.64	67.00	80.65
	800	18.25	14.20	68.87	83.07
	900	18.56	14 67	70 56	85.23
	1000	18.78	15.07	72.15	87.22
SO_2F_2	298.16	15.74	10.82	58.32	69.14
	400	18.36	12 42	61.73	74 15
	500	20.08	13.79	64 66	78.45
	600	21.36	14.95	67.28	82.23
	700	22.30	15.95	69.67	85.62
	800	22.96	16.77	71.82	88.59
	900	23.48	17.49	73.86	91.36
	1000	23.87	18.12	75 74	93.86

Discussion

As pointed out earlier for SOF_2 different assignments were made by different authors before a most accurate and reliable one was made by Pace & Samuelson (1966). The normal coordinate treatments made earlier have proved generally to be inconclusive. & Cotton Horrocks (1960) employed a potential involving five force constants which reproduced the frequency assignment made by O'Loane & Wilson (1955). On the other hand, the frequency assignment of Best & Trampe

(1938) was supported by a normal coordinate treatment carried out by Venkateswarlu & Sundaram (1957). The calculated frequencies using a modified UBFF have completely supported the vibrational assignment of Pace & Samuelson (1966).

In the case of SO_2F_2 the calculated frequencies here are not very close to the observed values. Hunt & Wilson (1962) with a total number of nine or less force constants made a number of calculations using different sets of vibrational frequencies and in no case they were able to converge to all the frequencies at one time. Using a Urey-Bradley force field (8 constants) the frequencies were calculated in the present investigation. Though the agreement between the observed and the calculated frequencies is not very good the set of force constants is a reliable one which compares well with the previous workers. It may be concluded that 9 or 8 force constant field is not a suitable one for SO_2F_2 and some additional interaction terms should be included.

From table 3 we see that the lone pair—bond pair repulsive force is not at all negligible in magnitude. The relative magnitudes of the lone-pair—bond-pair repulsion and bond-pair—bond-pair repulsions are also in accordance with the predictions of Gillespie & Nyholm (1957). The calculated mean amplitude quantities are comparable with the earlier results. The obtained ζ's for SO_2F_2 obey the sum rules given earlier.

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